(54) Title: CORROSION INHIBITORS FOR AQUEOUS SYSTEMS

(57) Abstract: A method of inhibiting corrosion in aqueous systems comprising adding to the system a composition comprising mono, bis and oligomeric phosphinosuccinic acid adducts and a method of preparing a composition comprising mono, bis and oligomeric phosphinosuccinic acid adducts comprising adding hypophosphite to fumaric acid slurry or solution in water to create a reaction mixture; and effecting a reaction by introducing a free radical initiator to the reaction mixture.

CORROSION INHIBITORS FOR AQUEOUS SYSTEMS

Field of the Invention

5   This invention relates to a new class of phosphinic acid-based corrosion inhibitors, to methods of preparing the inhibitors and to use of the inhibitors to inhibit corrosion in ferrous metal aqueous systems.

Background of the Invention

10   Ferrous metals, such as carbon steel, are one of the most commonly used structural materials used in industrial aqueous systems. It is well known that corrosion of the metal is one of the major problems in industrial aqueous systems having ferrous metal in contact with an aqueous

15   solution. Loss of metals due to general corrosion leads to deterioration of the structural integrity of the system because of material strength reduction. It can also cause other problems elsewhere in the system, such as under-deposit corrosion, reduction of heat transfer efficiency or

20   even blockage of the flow lines due to the transport and accumulation of corrosion products in places with low flow rates or geometric limitations.

      Corrosion inhibitors can be used to inhibit the corrosion of ferrous metals in aqueous or water containing

25   systems. These aqueous systems, include, but are not limited to, cooling water systems including open recirculating, closed, and once-through systems; systems used in petroleum production (e.g., well casing, transport pipelines, etc.) and refining, geothermal wells, and other

30   oil field applications; boilers and boiler water systems or

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systems used in power generation, mineral process waters
including mineral washing, flotation and benefaction; paper
mill digesters, washers, bleach plants, white water systems
and mill water systems; black liquor evaporators in the

5   pulp industry; gas scrubbers and air washers; continuous
casting processes in the metallurgical industry; air
conditioning and refrigeration systems; building fire
protection systems and water heaters; industrial and
petroleum process water; indirect contact cooling and

10 heating water, such as pasteurization water; water
reclamation and purification systems; membrane filtration
water systems; food processing streams and waste treatment
systems as well as in clarifiers, liquid-solid
applications, municipal sewage treatment systems; and

15 industrial or municipal water distribution systems.

        Localized corrosion such as pitting may pose even a
greater threat to the normal operation of the system than
general corrosion because such corrosion will occur
intensely in isolated small areas and is much more

20 difficult to detect and monitor than general corrosion.
Localized corrosion may cause perforation quickly and
suddenly without giving any easily detectable early
warning. Obviously, these perforations may cause leaks
that may require unscheduled shutdown of the industrial

25 aqueous system. Sudden failure of equipment due to
corrosion could also result in environmental damage and/or
present a serious threat to the safety of plant operations.

        Corrosion protection of ferrous metal in industrial
aqueous systems is often achieved by adding a corrosion

inhibitor. For example, many metallic ion corrosion
inhibitors such as
CrO_4^{2-}, MoO_4^{2-}, and Zn^{2+} have been used alone or in
combination in various chemical treatment formulations.

5   These inhibitors, however, have been found to be toxic and
detrimental to the environment and their use in open-
recirculation cooling water systems is generally
restricted. Inorganic phosphates such as orthophosphate
and pyrophosphate are also widely used. The inorganic

10 phosphates have been found to contribute to scale formation
(e.g., calcium phosphate, iron phosphate and zinc phosphate
salts) if used improperly.

In order to obtain satisfactory corrosion protection
and scale control at the same time, a robust treatment

15 program and frequent testing and monitoring to ensure
conformance are often required. Due to changes in water
chemistry (e.g., phosphates, pH, Ca^{2+}, etc.) or operating
conditions (e.g., temperature, flow rate, polymer dosages,
etc.), these requirements may be difficult to fulfill,

20 especially in systems with a long holding time index (e.g.,
>3 days).

"Holding time index" is a term used to define the
half-life of an inert species such as K^+ added to an
evaporative cooling system. Evaporative cooling systems

25 with a long holding time index put great demand on
treatment chemicals as these chemicals must remain stable
and function properly over long periods of time.

Orthophosphate and pyrophosphate are often used
together to provide optimal corrosion protection,

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especially against carbon steel pitting corrosion.
Orthophosphate is generally considered as an anodic
corrosion inhibitor. Pyrophosphate is considered as a
cathodic corrosion inhibitor.

5   It is well known that the combined use of an anodic
inhibitor and a cathodic inhibitor could provide
substantial synergistic benefits for reducing both
localized (i.e., pitting) and general corrosion.
Unfortunately, pyrophosphate is not stable in cooling water

10   systems as it reverts to orthophosphate via a hydrolysis
process. The reversion rate depends on many factors
including system holding time index, temperature, pH, metal
ion concentrations and bacteria activity. Furthermore, the
reversion rate in a system is generally not predictable.

15   In order to maintain satisfactory corrosion protection
performance, a certain level of pyrophosphate (e.g., >1.5
ppm p-PO$_4$) has to be maintained in the system by frequent
monitoring and activating product feed when the level is
lower than the specified value. Although this approach can

20   be successful, it has a number of major drawbacks.

     The drawbacks include the fact that maintenance of
pyrophosphate increases the dosage demand of polymer
dispersant and poses an even greater threat of phosphate
scale formation due to the presence of higher total

25   inorganic phosphate level in the water, especially when
"upsets" occur. Upsets in the context of the usage herein
refer to unanticipated changes in the concentration of
inorganic phosphate or sudden changes in pH, cycle of
concentration and substantial increase of temperature due

to non-steady state operations in cooling waters.
Furthermore, in some systems with very long holding time
index (HTI), maintaining a certain specified level of
pyrophosphate is often impossible with an acceptable

5 pyrophosphate feed dosage.

Some organic phosphonates, such as 2-phosphono-butane-
1, 2, 4-tricarboxylic acid (PBTC), 1-hydroxyethylidene-1,
1-diphosphonic acid (HEDP), and aminotrimethylene-
phosphonic acid (AMP) have also been used previously as

10 corrosion inhibitors alone or in combination with other
corrosion inhibitors in various chemical treatment
formulations. The effectiveness of these phosphonate base
treatments, however, is generally substantially lower than
the treatments based on inorganic inhibitors.

15 Some hydroxycarboxylic acids such as gluconic acid,
sacharic acid, citric acid, tartaric acid and lactobionic
acid have also been used in some treatment formulations.
The use of these acids, however, results in a major
challenge to control microbiological growth because these

20 hydroxycarboxylates are easily consumable nutrients for
bacteria growth. In addition, their corrosion inhibition
effectiveness is also much lower than the inorganic
corrosion inhibitors. Therefore, they are typically used
in low demand and easy to treat systems, such as some

25 comfort cooling systems.

U.S. Patent No. 4,606,890 discloses that 2-hydroxy-
phosphonoacetic acid (HPA) can be used as a corrosion
inhibitor in cooling water. HPA was found to be a much
more effective corrosion inhibitor than HEDP and PBTC (*See,*

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A. Yeoman and A. Harris, Corrosion/86, paper no. 14, NACE
(1986)). However, HPA is not halogen stable and it will
revert to orthophosphate in the presence of halogen based
biocides. Since bleach or NaOBr are the most widely used
5   biocides in cooling water systems, the halogen instability
of HPA limits its application potential and reduces its
effectiveness. In addition, HPA is found to be a
relatively ineffective $CaCO_3$ scale inhibitor.

In order to address some of the limitations of HPA, an
10   organophosphonic acid mixture has been used by many as mild
steel corrosion inhibitor in cooling water applications
(see, U.S. Patent No. 5,606,105). The active ingredients
of such inhibitors are a mixture of organophosphonic acids,
$H-[CH(COONa)CH(COONa)]_n-PO_3Na_2$, where $n<5$ and $n(mean)=1.4$,
15   hereinafter referred to as "PCAM". This mixture is halogen
stable under cooling water application conditions. In
addition, these organophosphonic acids are said to be a
better $CaCO_3$ scale inhibitor than HPA.

U.S. Patent No. 5,023,000 discloses and claims a
20   method for controlling the deposit of calcium carbonate
scale on the structural parts of a system exposed to
alkaline cooling water containing calcium carbonate under
deposit forming conditions. This patent addresses the
shortcomings to two counterpart patents GB No. 1,521,440
25   and U.S. Patent No. 4,088,678. These patents disclose the
preparation of monosodium phosphinicobis (succinic acid)
and related compounds. These organophosphinic acid
mixtures are prepared by reacting maleic acid with sodium
hypophosphite in the presence of a water soluble initiator.

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The optimum molar ratio of maleic acid to hypophosphite is
2.2. These references make it clear that further excesses
of maleic acid do not result in an improved product. In
contrast with the organophosphonic acids mentioned above,
5 these mixtures are comprised predominantly of a chemically
different type of organophosphorus compound, namely
organophosphinic acids. The salts of organophosphinic
acids are referred to as phosphinates.

U.S. Patent No. 5,018,577 discloses the use of a
10 predominantly phosphinate containing composition in oil
well applications, specifically in squeeze treatments for
the prevention and removal of scale from the surfaces of
oil wells and formation adjacent to the casings of these
wells.

15 Similarly, U.S. Patent No. 5,085,794 discloses the
reaction product of maleic anhydride, water and a
persulfate inhibitor for scale control noting that the
disclosed phosphinnicosuccinic acid oligomer is the
component deemed crucial as the active chelant or scale
20 inhibitor.

In all of these references citing the use of
organophosphinic acids produced from the reaction of
hypophosphite with maleic acid for control of scale
formation, it is the oligomer portion of the reaction
25 product of the maleic acid, hypophosphite and initiator
which is believed to be the key component for use as a
scale inhibitor. None of these references teaches the use
of the reaction product for a corrosion inhibitor in
aqueous systems. Furthermore, none of these references

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teaches a means to produce the desired organophosphinic
acids in a simple process that converts essentially all of
the hypophosphite and monomer raw materials into the
desirable organophosphinic acid products.

5   Given the shortcomings noted above, there is a need
for a more cost-effective corrosion inhibitor -- capable of
inhibiting both localized and general corrosion -- that is
environmentally benign and halogen stable, can maintain its
effectiveness in high stress (i.e., long HTI, high Ca^{2+},
10   etc.) conditions and can also prevent scale formation.

Summary of the Invention
        We have discovered an innovative and very effective
class of phosphinic acid-based organic corrosion
15   inhibitors. The phosphinosuccinic acid mixture of this
invention has all the desirable properties of a corrosion
inhibitor, and in particular, is a much more effective
corrosion inhibitor than PCAM, a traditional
organophosphonic acid mixture. Under certain conditions,
20   the phosphinosuccinic acid mixture is also more effective
than MoO_4^{2-}, VO_3^{3-} nitrite, HEDP, PBTC, AMP, polyacrylate,
phosphonosuccinic acid, orthophosphate, pyrophosphate and
gluconate. The phosphinosuccinic acid mixture is also as
effective as HPA.

25   The phosphinosuccinic acid mixture can also be
formulated with other components typically used in cooling
water treatment (e.g., polymer, orthophosphate, etc.) to
provide the most cost-effective corrosion control.

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Accordingly, in its principal aspect, this invention is directed to a method of inhibiting corrosion in aqueous systems comprising adding to the system a composition comprising mono, bis and oligomeric phosphinosuccinic acid adducts.

Detailed Description of the Invention

The phosphinic acid-based corrosion inhibitor of this invention are used to prevent corrosion of ferrous metals in aqueous systems, preferably industrial water systems including cooling water systems, petroleum systems or mineral process systems. The phosphinic acid-based corrosion inhibitors are added to the aqueous system in an amount of from 0.1 to about 10,000 ppm, preferably from about 0.2 to 100 ppm.

In a preferred aspect of this invention, the industrial aqueous system is a cooling water system.

The phosphinic acid-based corrosion inhibitors can be used alone or in combination with other ferrous metal corrosion inhibitors, yellow metal corrosion inhibitors, scale inhibitors, dispersants, biocides, and industrial aqueous system additives. Such a combination may exert a synergistic effect in terms of corrosion inhibition, scale inhibition, dispersancy and microbial growth control.

Representative corrosion inhibitors that can be used in combination with phosphinic acid-based corrosion inhibitors include, but are not limited to, phosphorus containing inorganic chemicls, such as orthophosphates, pyrophosphates, polyphosphates; hydroxycarboxylic acids and

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their salts, such as gluconic acids; glucaric acid; Zn^{2+}, Ce^{2+}; molybdates, vanadates, and tungstates; nitrites; carboxylates; silicates; phosphonates, HEDP and PBTC.

5   Representative yellow metal corrosion inhibitors that can be used in combination with the phosphinic acid-based corrosion inhibitors include, but are not limited to, benzotriazole, tolytriazole, mercaptobenzothiazole, halogenated azoles and other azole compounds.

        Representative scale inhibitors that can be used in
10   combination with the phosphinic acid-based corrosion inhibitors include, but are not limited to polyacrylates, polymethylacrylates, copolymers of acrylic acid and methacrylate, copolymers of acrylic acid and acrylamide, polymaleic acid, copolymers of acrylic acid and sulfonic
15 . acids, copolymers of acrylic acid and maleic acid, polyesters, polyaspartic acid, funtionalized polyaspartic acids, terpolymers of acrylic acid, and acrylamide/sulfomethylated acrylamide copolymers, HEDP (1-hydroxyethylidene-1,1-diphosphonic acid), PBTC (2-
20   phosphono-butane-1,2,4-tricarboxylic acid), AMP (amino tri(methylene phosphonic acid) and mixtures thereof.

        Representative biocides that can be used in combination with the phosphinic acid-based corrosion inhibitors include, but are not limited to, oxidizing
25   biocides, e.g., Cl_2, NaOCl, Br_2, NaOBr, chlorine dioxide, ozone, H_2O_2, sulfamic acid stabilized chlorine, sulfamic acid stabilized bromine, bromochlorohydantoin, cyanuric acid stabilized Cl_2 or Br_2, (e.g., trichloroisocyanurate and sodium bromide mixtures, dichloroisocyanurate and NaBr

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mixtures), or nonoxidizing biocides such as glutaraldehdye, isothiozolines (5-chloro-2-methyl-4-isothiazoline-5-one and 2-methyl-4-isothioazoline – 3-one), DBNPA or dibromonitropropianamide, terbuthylazine and quaterary

5   amine.

The phosphinic acid-based corrosion inhibitor of this invention is a composition comprising mono and bis and oligomeric phosphinosuccinic acid adducts of formulas I and II, respectively, as well as one or more oligomeric

10   species. While the mono and bis adducts of formula I and II are represented below as neutral, organophosphinic acid species, it is understood that the phosphinic and carboxylic acid groups may also exist in salt form. In addition to the phosphinosuccinic acids and oligomeric

15   species, the mixture may also contain some phosphonosuccinic acid derivatived from the oxidation of adduct I, as well as impurities such as various inorganic phosphorous byproducts of formula $H_2PO_2^-$, HPO_3^{2-} and PO_4^{3-}.

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              I   II
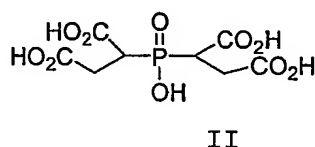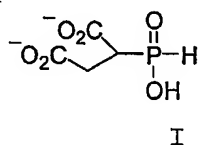
Possible structures for the oligomeric species are proposed in U.S. Patent Nos. 5,085,794, 5,023,000 and

25   5,018,577. In addition, the oligomeric species may also contain esters of phosphonosuccinic acid, where the phosphonate group is esterified with a succinate-derived alkyl group.

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The mono, bis and oligomeric components are typically characterized by a group of peaks in the proton decoupled phosphorus NMR spectrum in water at pH 5 as follows:

5   Mono: one peak between 26-29 ppm;
         Bis: two peaks between 30-35 ppm; and
         Oligomer: multiple peaks between 29-33 ppm.

         In a preferred aspect of this invention, the bis
10   adduct comprises from about 20 to about 85 mole percent
     based on phosphorous of the composition.
             The composition is prepared by (1) adding
     hypophosphite to a maleic acid or fumaric acid slurry or
     solution in water to create a reaction mixture; and (2)
15   effecting a reaction by introducing a free radical
     initiator to the reaction mixture. In the case of a
     slurry, the solids content is not critical as long as the
     slurry can be mixed. Typically, the slurry has a solids
     concentration of about 35-50% by weight.
20   "Hypophosphite" means hypophosphorous acid or a salt
     of hypophosphorous acid such as sodium hypophosphite.
             The reaction mixture is optionally heated, preferably
     at from about 40 °C to about
     75 °C, following addition of hypophosphite to affect
25   conversion to the desired phosphinosuccinic acid adducts in
     a reasonably short period of time.
             The reaction mixture may be partially or totally
     neutralized with base. A preferred base is aqueous sodium
     hydroxide which provides a slurry comprised of a maleic

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and/or fumaric acid salts. Other bases capable of forming
salts with fumaric or maleic acid, such as potassium
hydroxide and ammonium hydroxide, may also be used. The
base may be added before, after, or concurrently with the
5   hypophosphite.

Suitable free radical initiators include persulfates,
peroxides and diazo compounds. A preferred initiator is
ammonium persulfate. The initiator may be added to the
reaction mixture all at once or slowly introduced to the
10   reaction mixture over a period of several hours. The
initiator is preferably introduced to the mixture in an
amount of between about 10 to about 15 mole percent based
on hypophosphite.

In a typical prior art procedure for preparing
15   phosphinic acid compositions, maleic acid with hypohosphite
are used in a ratio of about 2:1. The reaction products
are predominately mono, bis and oligomeric
phosphinosuccinic acid adducts and inorganic phosphates as
described above.

20   We have unexpectedly discovered that if the reaction
is carried out with fumaric acid (*trans* 1,4-butanedioic
acid) instead of maleic acid (*cis* 1,4-butanedioic acid) the
ratios of mono, bis and oligomeric phosphinosuccinic acid
adducts are altered, resulting in a composition that
25   displays more effective corrosion inhibition properties
relative to the composition that is produced when maleic
acid is used under the same reaction conditions.

In particular, the fumaric acid-based process provides
a simple means to increase the amount of bis adduct in the

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composition and reduce the amount of byproducts in the composition due to a more efficient conversion of hypophosphite and fumaric acid raw materials into the desired phosphinic acids.

5   To achieve a similar result in the maleic acid process, a suitable form of maleic acid (such as maleic anhydride) must be added simultaneously with the initiator over the course of the reaction. These conditions are undesirable when carried out on a large scale as they

10   require either the use of specialized equipment to feed a solid reactant to the reactor, a prolonged manual addition of a solid reactant that increases worker exposure to the chemical reactants, or the addition of a comparitively large volume of monomer solution to the reactor that

15   dilutes the product to undesirable levels. In addition, the maleic acid-based process still cannot provide for the efficient conversion of essentially all of the hypophosphite and monomer (maleic or fumaric acid) reactants to the desired organophosphorous products.

20   The complete conversion of hypophosphite is important because it maximizes the yield of the desired products and minimizes the amount byproducts comprised of the relatively expensive hypophosphite and its oxidation products (inorganic phosphite and phosphate) that can otherwise

25   contribute to scale formation when the desired products are used to inhibit corrosion in aqueous systems.

          The complete conversion of monomer (maleic or fumaric acid) is important due to economic considerations (yield maximization) and due to the propensity for unreacted

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monomer to precipitate out from the product mixture to give a physically unstable product. Thus, the fumaric acid-based process of the instant invention gives a phosphinosuccinic acid product mixture with optimal

5 corrosion inhibiting properties in a manner that is more efficient and effective than previously disclosed processes.

The fumaric acid-based process is, in general, very similar to the maleic acid-based process except that

10 fumaric acid is used in place of maleic acid. Preferably, the fumaric acid is produced by isomerization of maleic acid. More preferably, the fumaric acid is prepared by hydrolyzing maleic anhydride in aqueous solution to prepare an aqueous solution of maleic acid which is then isomerized

15 using heat or a suitable catalyst to form an aqueous solution of fumaric acid.

The isomerization can be accomplished thermally only at high temperatures, so a catalyst is usually used to allow the reaction to proceed under relatively mild

20 conditions. Suitable catalysts for the transformation include thiourea and mixtures of oxidants and various bromine compounds. A preferred catalyst is a mixture of a bromide salt with a persulfate salt (US Pat. No. 3,389,173, *Ind. Eng. Chem. Res.* 1991, *30*, 2138-2143, *Chem. Eng.*

25 *Process.*, *30* (1991), 15-20). Preferably, a mixture of sodium bromide and ammonium persulfate is used to affect this transformation in aqueous media.

The aqueous fumaric acid solution is then converted to the phosphinic acid-based corrosion inhibitor of this

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invention by addition of hypophosphite and a radical
initiator to the fumaric acid solution as described above.
A preferred ratio of fumaric acid to hypophosphite in the
reaction mixture is about > 1.75-3. Preferably, the
5   initiator is added over a period of several hours while the
reaction mixture is heated at about 60 °C. The reaction is
then allowed to proceed until the hypophosphite is almost
completely converted to organophosphorous products.

        An advantage of this preferred process is that it is
10   more economical because it allows the use of inexpensive
maleic anhydride as a raw material instead of the more
expensive fumaric acid.

        Another advantage of the fumaric acid process is that
the total amount of residual inorganic phosphorous in the
15   product is typically less than three mole percent based on
total phosphorous.

        Accordingly, in another aspect, this invention is
directed to a method of preparing a composition comprising
mono, bis and oligomeric phosphinosuccinic acid adducts
20   comprising:
        i)   adding hypophosphite to fumaric acid acid slurry or
solution in water to create a reaction mixture; and
        ii)   -effecting a reaction by introducing a free radical
initiator to the reaction mixture.
25   In a preferred aspect, the reaction mixture is
prepared by converting an aqueous maleic acid slurry to an
aqueous fumaric acid slurry.

        In another preferred aspect, the reaction mixture has
a solids concentration of about 35-50% by weight.

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    In another preferred aspect, the reaction mixture is
neutralized with base.

    In another preferred aspect, the mole ratio of fumaric
acid to hypophosphite in the reaction mixture is about >
5   1.75-3.

    In another preferred aspect, the hypophosphite is
selected from the group consisting of hypophosphorous acid
or a salt of hypophosphorous acid.

    In another preferred aspect, the reaction mixture is
10   heated.

    In another preferred aspect, the free radical
initiator is slowly introduced to the reaction mixture over
a period of several hours.

    In another aspect, this invention is directed to an
15   aqueous composition comprising mono, bis and oligomeric
phosphinosuccinic acid adducts prepared by:
i)   adding hypophosphite to fumaric acid acid slurry or
solution in water to create a reaction mixture; and
ii)   -effecting a reaction by introducing a free radical
20   initiator to the reaction mixture.

    The foregoing may be better understood by reference to
the following Examples, which are presented for purposes of
illustration and are not intended to limit the scope of the
invention.

25   Example 1

    A 2.1/1 molar ratio of fumaric acid to hypophosphite
is used in this example. Crushed maleic anhydride
briquettes, 75.9 parts, are added to 104.4 parts water in a
1 liter resin flask equipped with a mechanical stirrer,

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condenser, nitrogen inlet, and heater. The anhydride is
allowed to hydrolyze at 40°C to give a maleic acid
solution. The reaction is then heated to 60°C and a
solution of sodium bromide (0.16 parts dissolved in 0.20

5   parts water) is added, followed immediately by a solution
of ammonium persulfate (0.43 parts dissolved in 1.49 parts
water). Within 60 minutes, an exothermic reaction ensues
that converts the maleic acid solution into 183.6 parts of
a 49.2 wt.% slurry of fumaric acid in water as verified by

10   proton NMR.

        Sodium hypophosphite monohydrate (38.9 parts) is added
to 182.6 parts of a 49.2 wt.% slurry of fumaric acid in
water contained in a 1 liter resin flask equipped with a
mechanical stirrer, condenser, nitrogen inlet, and heater.

15   A solution of ammonium persulfate (10.9 g dissolved in 36.9
parts water) is then added over a period of 5 hours while
the reaction temperature is maintained at 60°C under a
nitrogen blanket. The reaction solution is heated 1-5
hours further, and then adjusted to pH 6 under external

20   cooling with 96.2 parts of a 50% aqueous solution of sodium
hydroxide. Finally, 18 parts water is added. The product,
comprised of salts hypophosphite/fumarate adducts described
in the table below, displays the following molar
distribution of components, determined by phosphorous NMR

25   analysis. The first set of data represents the average of
four reactions run at 400-600 g scale according to the
procedure described above. The second set of data
represents a reaction carried out as described above except

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that the fumaric acid slurry is prepared by mixing fumaric
acid with water at a 126 g scale.

Component	Mole Percent
Phosphinicobis(succinic acid) salts (Structure II)	48, 45
Phosphinicosuccinic acid salts (Structure I)	17, 24
Phosphonosuccinic acid salts	8, 4
Phosphinicosuccinic acid oligomer salts (Structure III)	27, 27
Hypophosphite, phosphite, and phosphate salts	<1, <1

Example 2

A 2.5/1 ratio of fumaric to hypophosphite is used in
this Example. The reaction conditions are as described in
Example 1. The product, comprised of salts of
hypophosphite/fumarate adducts described in the table
below, displays the following molar distribution of
components determined by phosphorous NMR analysis.

Component	Mole Percent
Phosphinicobis(succinic acid) salts (Structure II)	49
Phosphinicosuccinic acid salts (Structure I)	7
Phosphonosuccinic acid salts	3
Phosphinicosuccinic acid oligomer salts (Structure III)	38
Hypophosphite, phosphite, and phosphate salts	<1

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Example 3

     This is a comparative example, using maleic acid
instead of fumaric acid at the same 2.5/1 mole ratio as
Example 2. It demonstrates that the results obtained with
5   fumaric acid are unanticipated. The first data set is the
results obtained in the lab using the general procedure
above, and the second data set is a plant run using the
same mole ratio maleic to fumaric.
The general reaction conditions described in Example 1 are
10   repeated except that maleic acid is substituted for fumaric
acid at the same molar concentration. The product,
comprised of salts of hypophosphite/maleate adducts
described in the table below, displays the following molar
distribution of components determined by phosphorous NMR
15   analysis.

Component	Mole Percent
Phosphinicobis(succinic acid) salts (Structure II)	
22, 17	
Phosphinicosuccinic acid salts (Structure II)	
24, 22	
Phosphonosuccinic acid salts	2,
12	
Phosphinicosuccinic acid oligomer salts (Structure III)	
43, 35	
Hypophosphite, phosphite, and phosphate salts	
5, 8	

Example 4

30   This example uses a low 1.75/1 ratio of fumaric to
hypophosphite. It does not yield >30% bis product and has a
higher level of undesirable inorganic phosphorous.

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The reaction conditions described in Example 1 are repeated except that a larger amount of hypophosphite is employed so that the molar ratio of fumaric acid to hypophosphite is 1.75/1. The product, comprised of salts of

5   hypophosphite/fumarate adducts described in the table below, displays the following molar distribution of components determined by phosphorous NMR analysis.

Component	Mole Percent

10   Phosphinicobis(succinic acid) salts (Structure II)
            30
      Phosphinicosuccinic acid salts   (Structure I)
            35
      Phosphonosuccinic acid salts   8
15   Phosphinicosuccinic acid oligomer salts (Structure III)
            22
      Hypophosphite, phosphite, and phosphate salts
            6

20   Example 5

      This example uses a 2.1/1 ratio of substantially neutralized sodium fumarate slurry demonstrating that the process works over a wide pH range by use of a salt fumaric acid. In this case, about 80% of the fumaric acid

25   carboxylic acids have been converted to the sodium carboxylate form, and the pH is raised from about 1 to about 6.

      Sodium hypophosphite monohydrate (13.0 g) is added to 61.0 of a 49.1 wt.% slurry of fumaric acid in water

30   contained in a 250 ml. resin flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and heater. Aqueous 50% sodium hydroxide, 32.1 g, is then added under

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mixing and cooling. A solution of ammonium persulfate (3.6

g dissolved in 6.0 g water) is then added over a period of

5 hours while the reaction temperature is maintained at

60°C under nitrogen blanket. The reaction solution is

5   heated 1-5 hours further, and 6 g water is added. The

product, comprised of salts of hypophosphite/fumarate

adducts described in the table below, displays the

following molar distribution of components, determined by

phosphorous NMR analysis.

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Component	Mole Percent
Phosphinicobis(succinic acid) salts (Structure II)	46
Phosphinicosuccinic acid salts (Structure I)	18
Phosphonosuccinic acid salts	8
Phosphinicosuccinic acid oligomer salts (Structure III)	26
Hypophosphite, phosphite, and phosphate salts	<1

Example 6

Step 1: Monosodium Phosphinocobis(dimethyl succinate)

A 2.1/1 molar ratio of dimethyl maleate to

25   hypophosphite is used in this example. Sodium

hypophosphite, 7.325 parts, are added to 6.25 parts water

and 12.5 parts ethanol in a resin flask equipped with a

magnetic stirrer, condenser, nitrogen inlet, heater and a

dropping funnel. This solution is heated to 80°C. A

30   solution consisting of 20.75 parts dimethyl maleate, 0.86

parts benzoyl peroxide(70% solution) and 25 parts ethanol

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is then added dropwise to the reaction flask over a period
of 4.75 hours. The reaction mixture is heated for an
additional 15 minutes then cooled. The solvent is removed
by rotary evaporation under reduced pressure.

5

Step 2: Sodium Phosphinocobis(succinate)

     34.5 parts of monosodium phosphinocobis(dimethyl
succinate) are added to 20 parts water and 55.4 parts of a
50% aqueous solution of sodium hydroxide in a reaction

10 flask equipped with a magnetic stirrer, condenser, and
heater. The reaction is heated to 100°C and maintained at
that temperature for 2 hours. The product is diluted with
20 parts water and then neutralized with 40.4 parts
hydrochloric acid to about pH 6.

15   The product, comprised of salts of
hypophosphite/maleate adducts described in the table below,
displayed the following molar distribution of components
determined by phosphorous NMR analysis.

20 Component   Mole Percent

Phosphinicobis(succinic acid) salts   (Structure II)
               88
Phosphinicosuccinic acid salts   (Structure I)
              9
25 Phosphonosuccinic acid salts   1
Hypophosphite, phosphite, and phosphate salts
     2

Example 7

30   Electrochemical Tests to determine corrosion rate For
Tables 1 - 3.

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A pre-polished carbon steel (mild steel, C1010 or C1008)
cylindrical tube (length=0.5 in, outer diameter =0.5 in,
area = 5 cm^2) sealed with MICROSTOP STOP-OFF^{TM} lacquer
(Pyramid Plastic Inc.) and installed on a Pine rotator is

5   used as the working electrode. The electrode is polished
with a 600 grit SiC sand paper, washed with acetone and
deionized water, and dried with a piece of clean Kimwipes^{TM}
before applying the lacquer. Then the electrode is placed
in the air for ~15 minutes to allow the paint to dry before

10   immersion. The counter electrode is two high density
graphite rods. A saturated calomel electrode or a Ag/AgCl
electrode is used as the reference electrode. Solution
Ohmic drop is minimized by placing the small Luggin
capillary opening about 1~2 mm from the working electrode

15   surface. A.C. impedance experiments shows that the ohmic
drop in the low corrosion rate conditions (e.g., R_p > 3000
ohm cm^2 or < 7 ~ 9 mpy) usually contributed to not greater
than 10% of the total measured polarization resistance (R_p).
        Test cells holding 700 ml ((for Table 3, 10.8 liters)

20   solution are used in the tests. The test solutions are
prepared from deionized water, analytical grade chemicals
and chemicals synthesized according to the method described
in this invention. The solution is aerated and allowed to
come to thermal and chemical steady-state (typically ~ 0.5

25   hours) before immersing the working electrode. All the
openings of the cell are covered with either a rubber plug
or Saran Wrap^{TM} to minimize solution loss due to
evaporation. The loss due to evaporation is usually less
than 10% in 24 hours. The bench-top corrosion tests are

conducted at 38°±0.3°C, or 48.9°±0.3°, unless specified
otherwise. A pH controller controlled the pH of the test
solution by feeding either dilute H_2SO_4 or CO_2 gas (CO_2 is
used only in the tests listed in Table 3). The test
5   solutions are also aerated by purging with air during the
tests.

A Gamry potentiostat and Gamry corrosion software are
used to conduct the electrochemical measurements. After
>16hours immersion, the polarization resistance of the
10 electrode is determined by imposing a small overpotential
(±15mV versus E_{corr}) on the working electrode and measuring
the resulting current under steady state conditions. Quasi-
steady-state potentiodynamic cathodic and anodic scans
(e.g., 0.5mV/sec) are conducted immediately after the
15 polarization resistance measurement. These measurements are
commenced at the corrosion potential and polarized up to
200mV in either cathodic or anodic direction. The cathodic
branch is recorded first. The anodic scan is conducted ~0.5
hours after the completion of the cathodic scan. The
20 surface area averaged (or general) corrosion rates are
determined from extrapolation of either the anodic branch
or cathodic branch of the linear log(i) versus potential
region of the polarization curve to the corrosion potential
or are determined from the polarization resistance with the
25 use of the Stern-Geary equation. The Tafel slopes of
200mV/dec for both anodic and cathodic polarization curves
determined from the average values of several quasi-steady-
state potentiodynamic scans measurements and prior
experience are used to calculate the general corrosion

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rates from the measured polarization resistances. The
corrosion rates shown in the Tables 1-3 are calculated as
the average of polarization resistance rate, anodic Tafel
and cathodic Tafel extrapolation rates.

5   In some cases (i.e., the results in Table 3 and the
results at 100F in Table 1), the carbon steel electrodes
are first prepassivated in 0.5 wt% sodium benzoate solution
for 2 to 20hr at the test temperature before immersing in
the test cell. No significant differences (e.g., corrosion

10   rate differences are less than 20 - 30% from each other)
are noted in the corrosion rates obtained from the
different sample preparation methods described here under
comparable test conditions.

      All solutions are prepared by using analytical grade

15   chemicals, commercially available products, or compounds
synthesized according to the procedure described in the
instant invention.

Table 1
Corrosion Inhibitor Screening Test Results
- Hard Water

360ppm $CaCl_2$, 200ppm MgSO4, 100ppm $NaHCO_3$,
pH=8.4, 120 °F, 160rpm; 16 hours immersion

Compound	Dosage as Active in Acid Form or Stated	MS General Corrosion Rate (mpy)
Blank	None	43.50
Orthophosp hate	15ppm as PO_4	17.35
Pyrophosph	30ppm as PO_4	11.99

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ate
HPA            15ppm              2.13
               30 ppm             2.47        Av.
                                              of 3
                                              tests


PCAM           15ppm              15.43
PCAM           20ppm              6.26
PCAM           30ppm              23.68
PCAM           40ppm              15.28       Av.
                                              of 6
                                              tests

Example 1      15ppm             2.78
Example 1      20ppm             2.16
Example 1      30ppm             0.97
Example 1      40ppm             2.17        Av.
                                              of 2
                                              tests

HEDP           15ppm             13.05
HEDP           30ppm              8.09
AMP            15ppm             9.25
AMP            30ppm             16.11
PBTC           15ppm             6.17
PBTC           30ppm             10.49
Polyacryla     15ppm             11.84
te
(MW=2000)
Polyacryla     30ppm             34.49
te
(MW=2000)
Molybdate      15ppm as MoO4     19.89
Vanadate       15ppm as VO3      17.43
Nitirte        30ppm as NO2      9.38
Zn2+           5ppm as Zn        37.24
Gluconate      30ppm             5.69
Phsophonos     15ppm             6.80
uccinic
acid
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Zn^{2+}

Blow results are obtained at 100 °F

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Blank          None              21.5        Av.
                                              of 2
                                              tests
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Example 1	40ppm		0.98	Av. of 2 tests
Example 1 + Polymer 1	40ppm Example 1 + 10ppm Polymer 1		0.92	Av. of 3 tests
PCAM + Polymer 1	40ppm PCAM + 10ppm Polymer 1		19.50	Av. of 3 tests

Note: HPA = 2-hydroxy-phosphonacetic acid

PCAM = phosphonocarboxylic acid mixture, $H-[CH(COOH)CH(COOH)]_n-PO_3H_2$, where $n<5$ and $n_{mean}=1.4$

HEDP = 1-hydroxyethylidene-1,1-diphosphonic acid

AMP = Amino tri(methylene phosphonic acid)

PBTC = 2-phosphono-butane-1,2,4-tricarboxylic acid

Polymer 1 = Acrylic acd (50 - 60 mole%)/acrylamide (20-36 mole%)amino methane sulfonate (14-20%) terpolymer

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The results in Table 1 show that the compounds of this invention (i.e., example 1) are much more effective mild steel corrosion inhibitors than PCAM. The compound of Example 1 is also more effective than MoO_4^{2-}, VO_3^{3-} ,

5   nitrite, HEDP, PBTC, AMP, polyacrylate, phosphonosuccinic acid, o-PO_4, p-PO_4 and gluconate. It is as effective as HPA. In the presence of a phosphate dispersant polymer (polymer 1, commonly used in cooling water systems to prevent scale formation), The compound of Example 1 is still a more

10   effective mild steel corrosion inhibitor than PCAM.

Table 2

Corrosion Inhibitor Screening Test Results: The Effect Composition Changes

Treatment ID	Treatment Composition (based on P^{31} NMR Results)					MS General Corrosion Rate (mpy)		Note
	Mono Adduct (%)	Bis adduct (%)	Oligomer (%)	Ing P (%)	PSA (%)	15ppm Treatment	30ppm Treatment	
A	34	17	35	8	5	11.9	17.7	
B	66	15	0	18	1	11.8	3.16	
C	65	15	0	20	0	5.72	5.78	
D (example 1)	15	49	28	<1	7	2.78	0.97	
E	19	45	29	1	6	2.16 (20ppm)	2.17 (40ppm)	
F	0	43	27	0	27	2.69	N/A	3% Unidentified
G	0	0	60	3	31	21.1	9.2	6% Unidentified
H	9	0	56	4	15	6.9	12.2	18% Unidentif ed
PSA	0	0	0	0	100	6.8	27.1	
PCAM	0	0	0	0	60	15.4	23.6	
Blank	0	0	0	0	0	43.5		

Hard Water: 360ppm CaCl$_2$, 200ppm MgSO$_4$, 100ppm NaHCO$_3$, (all as CaCO$_3$),   pH=8.4, 120F, 160rpm, 16 hours immersion

Table 3

Corrosion Inhibitor Screening Test Results: The Effect of Composition Changes

Conditions: 40ppm total inhibitor concentration except for the blank test, which has no inhibitor
C1008 Electrode, 360ppm CaCl2, 200ppm MgSO4, 100ppm NaHCO3, (all as CaCO3),
pH=8.4, 100F, 160rpm, 24 - 72 hours immersion.

Treatment	Treatment Composition based on P31 NMR results					MS General Corrosion Rate (mpy)
	Mono Adduct (%)	Bis adduct (%)	Oligomer (%)	Ing P (%)	PSA (%)	
I	25	36	31	1.2	7	0.98
J	15.9	42	34.6	0.8	6.7	1.82
D (Example 1)	15	49	28	<1	7	1.36
50% D + 50% K	12	68.7	14	1.3	4	2.70
25% D + 75% K	10.5	78.6	7	1.2	2.5	1.83
K	9	88.4	0	1.6	1	7.67
Blank	0	0	0	0	0	21.5

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The data in Tables 2 and table 3 show that (1)
mixtures of phosphinosuccinic acid adducts, comprising
various percentages of mono, bis and oligomeric adducts,
are effective mild steel corrosion inhibitor; and (2) the
5   best corrosion inhibition activity will be obtained if the
bis adduct has a percentage ranging from more than ~17% to
less than 88%.

While the principles of the invention have been shown
and described in connection with but a few embodiments, it
10   is to be understood clearly that such embodiments are by
way of example and are not limiting.

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CLAIMS

1.   A method of inhibiting corrosion in aqueous systems comprising adding to the system a composition comprising mono, bis and oligomeric phosphinosuccinic acid adducts.

2.   The method of claim 1 wherein the bis adduct is present in the reaction product in amounts ranging from 20-85 mole percent based on phosphorous.

3.   The method of claim 1 wherein the aqueous system is an industrial aqueous system.

4.   The method of claim 1 wherein the industrial aqueous system is a cooling water system.

5.   The method of claim 1 further comprising adding to the aqueous system an effective amount of one or more ferrous metal corrosion inhibitors, yellow metal corrosion inhibitors, scale inhibitors, dispersants, biocides, and industrial aqueous system additives.

6.   A method of preparing a composition comprising mono, bis and oligomeric phosphinosuccinic acid adducts comprising:

i)   adding hypophosphite to fumaric acid slurry or solution in water to create a reaction mixture; and

ii)   -effecting a reaction by introducing a free radical initiator to the reaction mixture.

7.   The method of claim 6 wherein the reaction mixture is prepared by converting an aqueous maleic acid solution to an aqueous fumaric acid slurry.

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8.   The method of claim 6 wherein the reaction
mixture has a concentration of about 35 to about 50
percent by weight of fumaric acid.

9.   The method of claim 6 further comprising
5   neutralizing the slurry.

10.   The method of claim 6 wherein the mole ratio of
fumaric acid to hypophosphite in the reaction mixture is
about > 1.75-3.

11.   The method of claim 6 wherein the hypophosphite
10   is selected from the group consisting of hypophosphorous
acid or a salt of hypophosphorous acid.

12.   The method of claim 6 further comprising heating
the reaction mixture.

13.   The method of claim 6 wherein the free radical
15   initiator is slowly introduced to the reaction mixture
over a period of several hours.

14.   An aqueous composition comprising mono, bis and
oligomeric phosphinosuccinic acid adducts prepared
according to the method of claim 6.

20   15.   The aqueous composition of claim 14 wherein the
bis adduct is present in the reaction product in amounts
ranging from 30-80 mole percent based on phosphorous.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/05598

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7)   :C02F 5/00,5/14; C09K 15/06, 15/32

US CL   : 210/697,699; 252/389.23,389.24,400.23,400.24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :   210/697,699; 252/389.23,389.24,400.23,400.24,387,397,80,82; 422/12,13,15

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPAT in WEST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,023,000 A (KNELLER et al.) 11 June 1991, see abstract, column 5, lines 34-42 ,and samples 1, 3, and 7 in Table II.	1-5, 14-15
X	US 5,085,794 A (KNELLER et al.) 04 February 1992, see abstract, and samples 3, 7, and 9 In Table II.	1-5, 14-15
X	US 5,018,577 A (PARDUE et al.) 28 May 1991, see abstract, and Tables 1-8.	1-5, 14-15
X	US 4,088,678 A (MATT et al.) 09 May 1978, see abstract, column 2, lines 1-28 and the examples.	1-5, 14-15
X	GB 1 521 440 A (NALCO CHEMICAL COMPANY) 16 August 1978, see page 2, lines 1-65	1-15

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
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"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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